

ENVIRONMENTAL PROTECTION

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UTILIZATION OF GALVANIC SLIME IN PRODUCTION OF CONSTRUCTION MATERIALS

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A possibility of utilization of galvanic slime in production of brick is investigated. The properties of obtained samples meet the international standard requirements.

Recycling of waste is becoming an urgent issue and the basis for finding resource-saving solutions. By recycling waste, decreasing the use of natural resources, reducing waste emissions and discharges, and removing the toxic effect of waste storage on the environment, one can solve a vast number of economic and environmental problems. However, the majority of waste in the Republic of Belarus are currently accumulated at dumping grounds, at factories, or in unauthorized places, which, as a rule, do not meet sanitary and hygienic requirements. Thousands of hectares of land are removed from economic use in order to store waste. Waste concentrated in waste depositories, on dumping grounds, or in slime pits is a source of contamination for surface and subsurface waters, air, and soil; heavy metals are observed to migrate into soil and vegetation [1]. Waste-storage facilities require substantial expenditures. At the same time, wastes contain valuable components, whose extraction and utilization would make it possible to ensure waste safety and to save natural resources.

The waste utilization level in Belarus remains extremely low. Thus, halite waste is recycled to the extent of 6.6%, argillaceous-salt slime is not utilized; 624 million tons of potassium production waste is accumulated in slime pits and dumping grounds; the level of utilization of other large-volume waste is decreasing: that of hydrolyzed lignin to 20.2%, and that of phosphogypsum to 0.4%. Liquid sewage in Belarus after biological purification is not utilized and becomes accumulated on silt grounds and in ponds. The most complex problem is the utilization of highly toxic waste products that have a complex chemical composition and contain a substantial amount of heavy metals, for instance, galvanic slime.

The construction materials industry is of special importance in treating this problem, since it can use different waste generated by other sectors of industry. These waste products include slag and ash from power plants, metallurgical slag, galvanic slime, phosphogypsum and similar compounds, stripping rocks generated in mining coal, iron ore, nonferrous metal ores and other minerals, pyrite cinders, red slime from alumina production, sawdust, etc. [2, 3]. Accordingly, the range of waste-based materials and products is extensive. Therefore, the problem of quality control of the waste-based products becomes topical.

The present study investigated the possibility of utilization of galvanic slime in ceramic brick production. Galvanic slime is an inorganic waste product resulting from reactant purification of galvanic sewage, which is characterized by a complex chemical composition and high toxicity owing to its content of heavy metals. The material selected for investigation was galvanic slime from the BelVAR JSC (Minsk) with the following composition (here and elsewhere wt.% is indicated): 10.78 SiO₂, 2.73 Al₂O₃, 12.90 Fe₂O₃, 0.33 FeO, 0.21 TiO₂, 1.08 Cr₂O₃, 0.46 NiO, 27.85 CaO, 1.42 ZnO, 7.09 CuO, 2.12 MgO, 0.88 K₂O, 2.18 Na₂O, 1.75 SO₃, and 28.21 calcination loss.

The phase composition of the slime was investigated using x-ray phase analysis. The identification of the interplanar distances made it possible to identify calcite CaCO₃, quartz SiO₂, heavy metal hydroxides, hematite Fe₂O₃, and chromium oxide Cr₂O₃ in the slime sample. The chemical and phase composition of galvanic slime indicates that it can be used as an additive for improving the physicomaterial properties of materials in the production of construction silicate materials.

The experimental samples of brick were made from the following materials: clay from the Gaidukovskii deposit,

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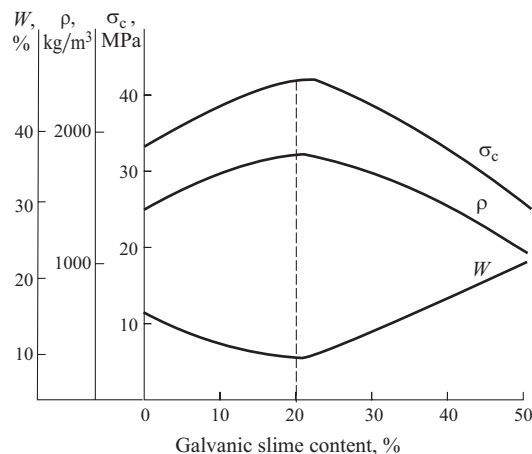


Fig. 1. Water absorption W , density ρ , and compressive strength σ_c of samples versus the galvanic slime content.

quartz sand, and galvanic slime from the BelVAR JSC. The amount of slime introduced in mixtures varied from 0 to 50%. Water was added to the mixture if needed, then the mixture was held to improve its molding properties and to homogenize its composition. All experimental compositions had good molding properties.

Brick samples were molded in a metal mold of size $30 \times 60 \times 15$ mm, dried naturally, and fired in an electrical furnace. The main technical characteristics of the waste-containing bricks were water absorption, apparent density, porosity, shrinkage, and compressive strength.

Analysis of the obtained results indicated that introduction of up to 20% galvanic slime improves the physico-mechanical properties of bricks (Fig. 1). This may be related to the emergence of new crystalline phases, such as anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ and diopside $\text{CaMgSi}_2\text{O}_6$ that have high physico-mechanical parameters. Furthermore, CaO entering in reactions with the main components produces low-melting eutectic melts in the form of aluminocalcium silicate glasses, thus improving the cohesion of the material and decreasing its shrinkage, which also contributes to improving the physico-mechanical properties of the product. The presence in the slime of such fluxes as Na_2O and K_2O facilitates the emergence of low-melting aluminosilicate glass melts. However, when the galvanic slime content is over 20%, at a temperature of $850 - 900^\circ\text{C}$ a substantial amount of CO_2 is released, which is formed in dissociation of CaCO_3 , which is the main component of the slime. This process has a loosening effect on the material structure; consequently, a slime content above 20% increases the porosity and water absorption, which worsen the physico-mechanical properties of the samples.

It should be noted that a decrease in air shrinkage from 6.0 to 3.5% upon the introduction of galvanic slime indicates a decrease in drying and firing sensitivity, which makes it possible to accelerate these processes without cracking the brick.

Thus, the optimum mixture composition is as follows (%): 60 clay, 20 galvanic slime, and 20 sand as the grog addi-

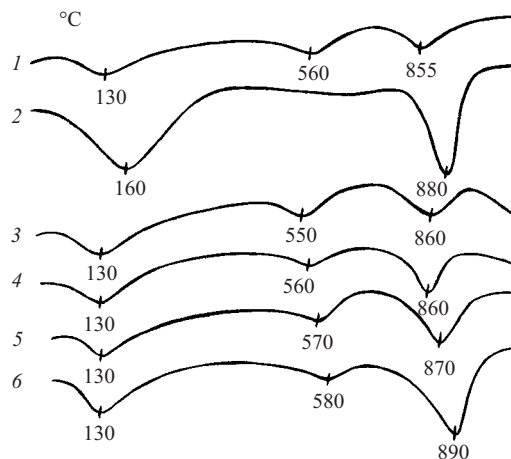


Fig. 2. Differential thermal analysis curves of experimental samples: 1) mixture without waste; 2) galvanic slime; 3, 4, 5, and 6) mixture bearing, respectively, 10, 20, 30, and 40% waste.

tive. The optimum firing temperature (1000°C) was selected on the basis of the experimental data obtained in heat treatment of samples at temperatures of 800, 900, 1000, 1100, and 1200°C .

The optimum composition samples have compressive strength of 42 MPa, apparent density 1800 kg/m^3 , water absorption 13%, apparent porosity 24%, air shrinkage 3.5%, and fire shrinkage 4% and meet the requirements of the GOST 530–95 standard.

However, an obligatory requirement imposed on the production of any material containing any waste (especially toxic waste) is the environmental safety of such material. Therefore, before recommending large-scale use of galvanic slime in the production of building materials, this waste was studied in accordance with the ISO 14000 international standard that evaluates the impact of a material on the ambient environment in all stages, starting with the extraction and preparation of waste and ending with the service of the finished product.

When the waste is utilized, its impact on the ambient environment decreases, as fewer raw materials have to be produced, which reduces the load on the stage of transporting materials to a production site. However, the stage of preparation for the utilization and transportation of waste should be considered separately. It is necessary to provide waste transportation methods, which would have a minimum negative effect on the environment. Thus, the present study proposes granulation of galvanic slime and its transportation in special sealed containers.

The main problem in production of building materials using toxic waste may arise at the stage of firing. The process of firing bricks containing galvanic slime was investigated using the differential thermal analysis (DTA) data, which indicated an increase in emission of carbon monoxide manifested in an increased endothermic effect at $850 - 900^\circ\text{C}$ (Fig. 2). The mechanically bonded water from argillaceous

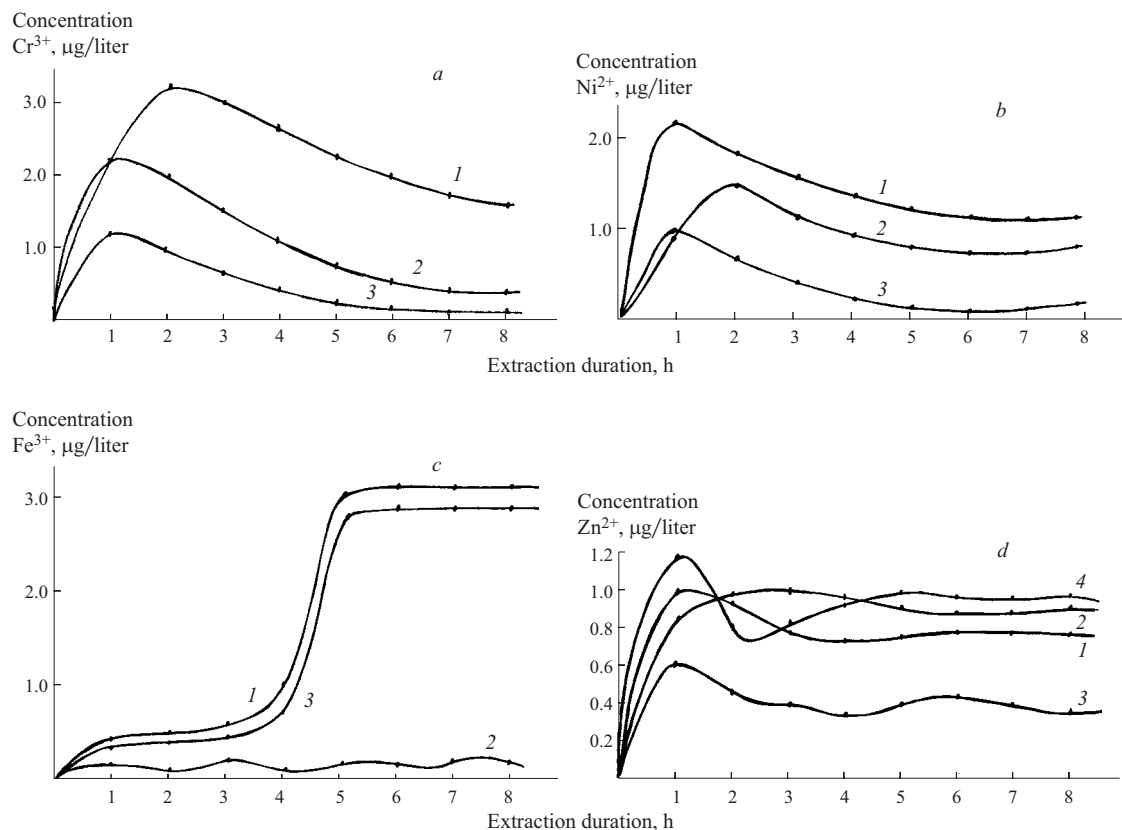


Fig. 3. Kinetics of extraction of Cr^{3+} (a), Ni^{2+} (b), Fe^{3+} (c), and Zn^{2+} (d) from brick samples in different media: 1) sample bearing 20% galvanic slime, acid medium, pH = 4; 2) neutral medium, pH = 7; 3) sample without galvanic slime) acid medium, pH = 4; 4) alkaline medium, pH = 10.

colloids is removed in the temperature interval of 130–160°C. The endothermic effect at 550–570°C is absent in the waste sample, since it is inherent in the argillaceous component, namely, the process of water removal from argillaceous minerals accompanied by weight loss and shrinkage. When slime is introduced, this effect is shifted toward higher temperatures, which delays to some extent the dehydration process. This is presumably due to the screening effect of the finely disperse waste.

The third endothermic effect within the temperature interval of 850–890°C is present both in the initial mixture and in the mixture with the waste. The effect is related to decarbonizing of carbonate components, mainly CaCO_3 , and is more evident in the waste sample: the effect here has a sharp maximum and is deeper. Introduction of galvanic slime in an argillaceous mixture shifts the temperature interval of this endothermic effect toward higher temperatures (up to 890°C). At the same time, the surface area of this thermal effect increases, which points to an increase in the content of the calcium-bearing component in the mixture and an increase in the quantity of carbon monoxide formed.

Thus, introduction of galvanic slime into a mixture does not modify the qualitative composition of emissions in firing but increases the amount of carbon monoxide released.

The service period of the brick produced using galvanic slime may present the most significant environmental risk. There is yet no generally accepted method for estimating the environmental safety of such products. The present study proposes to evaluate environmental safety based on the service conditions of the product.

A brick in service does not contact a highly aggressive medium or food products; it is only subjected to the effect of atmospheric moisture. Since the possibility of release of toxic compounds into the ambient medium depends only on their degree of solubility, the quality of the building materials should be such that the concentration of toxic elements in their extract does not exceed the maximum permissible concentration for these compounds.

As the atmospheric moisture effect at elevated temperatures ensures the maximum concentration of heavy metals in an extract, environmental safety control was carried out taking into account the GOST 10134–82 standard, which provides for crushing building materials and obtaining extracts over a water bath at a temperature of 100°C. According to the testing method proposed by us, the experiments were carried out in different media: acid (pH = 4), alkaline (pH = 10), and neutral (pH = 7), and the pH level in these media was maintained by the buffer solutions. Extraction lasted for 8 h, and samples were taken each hour and analyzed for the pres-

TABLE 1

Extraction object	Concentration of heavy metal ions 8 h after extracting in an acid medium (pH = 4), µg/liter			
	Cr ³⁺	Ni ²⁺	Fe ³⁺	Zn ²⁺
Galvanic slime	200.0	105.0	290.0	110.0
Sample with 20% galvanic slime	1.6	1.2	3000.0	0.7
Sample without galvanic slime	0.2	0.4	2800.0	0.3

ence of heavy metals using the atom-absorption method. For reference purposes, an identical analysis was performed for samples without galvanic slime, samples with slime, and slime samples.

The experimental data on the whole indicate a substantial decrease in the mobility of heavy metal ions introduced into the mixture, compared with the mobility of these ions in slime (Table 1); the highest mobility was registered in the acid medium, except for zinc ions (Fig. 3).

The high concentration of iron ions in extracts is related to a high content of iron in the initial materials. It is known that the Belarus materials are rich in ferric oxide; therefore, its content is high even in samples not bearing galvanic slime. This is corroborated by the extraction data for a reference sample consisting of crushed brick without galvanic slime (Fig. 3c, curve 3).

It can be seen in Fig. 3d (curve 4) that the recovery of zinc is most intense in an alkaline medium. According to the published data [4], under high alkaline conditions with pH exceeding 10 or 11, hydrocomplexes of $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Zn}(\text{OH})_4^{2-}$, which contain water molecules in their coordination sphere, are formed and lead to an enhanced concentration of zinc under alkaline conditions. Cations of other metals in the alkaline medium are found in trace quantities.

The experiment did not supply reliable data on the behavior of heavy metals in brick samples. X-ray phase analysis was not able to identify any crystalline phases containing

heavy metals. This can be due to the absence of such phases, or to the low sensitivity of the x-phase analysis. If such phases are absent, it can be assumed that the heavy metal ions pass over to the vitreous phase of the ceramic brick and are incorporated between the silicon-oxygen tetrahedra, which ensures their strong bonding and low mobility. However, it is also possible that the heavy metal ions are bonded in difficultly soluble compounds (silicates and aluminosilicates) that have a high stability and, consequently, heavy metals in this form are characterized by a low mobility as well.

It is established that the mobility of heavy metal ions in both cases is lower than their mobility in galvanic slime, which is corroborated by the experimental data, and the concentration of these metals in the extracts is significantly below the maximum permissible concentration.

Thus, the obtained data point to the possibility of utilizing galvanic slime in brick production. The production of construction materials using galvanic slime is an efficient method for utilization of this waste and allows for an expansion of available resources for producing construction materials.

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